

OVERVIEW OF THE REACTIVITY OF ORGANICS IN SUPERHEATED WATER: GEOCHEMICAL AND TECHNOLOGY IMPLICATIONS

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ABSTRACT

The reactivity of organic molecules in hot water is a field of chemistry developing from studies aimed at understanding how organic matter (kerogen) forms in natural environments and then breaks down into energy source materials. In natural systems where kerogens are depolymerized, water is ubiquitous and hot and usually contains salt and minerals. Reactions such as cleavages and hydrolyses in these media are facilitated by changes in the chemical and physical properties of water as temperature increases. These changes make water more compatible with the reactions of organics. We will present a brief geochemical background, discuss chemical and physical properties of water, key features of known kerogen structural models and the aqueous chemistry of cleavage and hydrolysis reactions involved in kerogen depolymerization. Based on the understanding of the roles of water as a solvent, reagent and catalyst, potential applications in areas such as plastics recycling and synthesis of chemicals will be described.

INTRODUCTION

This article describes an emerging area of chemistry: the reactivity of organic compounds in superheated water. We begin with a brief geochemical background and then discuss the implications of the aqueous chemistry to understanding the formation of oil from the solid, insoluble, organic material (kerogen) in resources such as shale and coal. Finally, we point out potential implications to more technological areas such as plastics recycling.

Common organic molecules that were previously considered unreactive in liquid water undergo many chemical reactions when the temperature is increased to 250-350 °C; these reactions were previously expected only in the presence of strong acid or base. For example, ethers and esters, which are unreactive to heat alone, undergo facile cleavage and hydrolysis, respectively, in water at 250-350 °C.¹ Ethers and esters are major cross-links in several oil shale kerogens and are illustrated in a portion of the detailed structural model of a Rundle Ramsay Crossing Type I kerogen in Figure 1. Analogously, polyethylene terephthalate polymers (found in plastic soft drink bottles) can be hydrolyzed quantitatively back to their starting materials in superheated water in less than an hour.² Other polyesters, and also polyamides (like nylon), are equally susceptible to hydrolysis. A major analogy to such polymer degradation reactions in nature is catagenesis: the process by which solid petroleum source rock kerogens, which are cross-linked macromolecular structures, are converted into liquid petroleum. Natural catagenesis takes place at temperatures below 200 °C over millions of years in aqueous environments at pressures of about 600 atmospheres. Because of the relatively low temperatures, it has been hypothesized that some of the chemistry by which petroleum is formed is catalyzed by clay minerals in the formations.³ Recent studies in our laboratories have made it clear that two additional factors can affect and catalyze the kerogen depolymerization chemistry that leads to petroleum formation. One factor is that simple aqueous chemistry generates water-soluble products that are acidic or basic, or have redox properties. The other factor involves the salts present in sea water or aqueous environments.^{4,5}

High temperature water under autogenic pressure provides a significantly more favorable reaction medium for ionic reactions of non-polar organic compounds than does water up to its boiling temperature (Table 1). At 300 °C, water exhibits a density and polarity similar to those of acetone at room temperature.⁶ The dielectric constant of water drops rapidly with temperature, and at 300 °C has fallen from 80 (at 20 °C) to 2⁷ and its solubility parameter decreases from 23.4 to 14.5 cal/cm.⁸ This means that, as the water temperature is increased, the solubility of organic compounds increases much more than expected for the natural effect of temperature. Furthermore, the negative logarithmic ionic product of water at 250 °C is 11, and of deuterium oxide is 12, as compared to 14 and 15, respectively, at 20 °C.⁹ This means that water becomes both a stronger acid and a stronger base as the temperature increases. Therefore, in addition to the natural increase in kinetic rates with temperature, both acid and base catalysis by water are enhanced at higher temperatures.

**Table 1. Chemical/Physical Properties of Superheated Water Become
More Compatible to Reaction with Organics
at High Temperature**

T (°C)	Density (g/cm ³)	Dielectric Constant	Solubility Parameter (cal/cm ³) ^{1/2}	-logKw	Vapor Pressure (psi)
25	0.997	78.85	23.4	13.99	23.8
150	0.917	43.89	20.6	11.64	69.0
200	0.863	34.59	19.0	11.30	225.5
250	0.799	26.75	17.0	11.20	576.6
300	0.713	19.66	14.5	11.30	1245.9
350	0.572	12.61	10.3	-----	2397.8

Geochemical Background

Jurg and Eisma¹⁰ reacted samples of behenic acid ($n\text{-C}_{21}\text{H}_{43}\text{COOH}$) with the acidic clay mineral, montmorillonite, in sealed tubes in the presence and absence of water at 200 °C for 89 and 760 h. They found significant hydrocarbon formation only in the presence of the clay catalyst. The ratios of iso- to normal-butane (1:40) and iso- to normal-pentane (1:40) were raised significantly in the presence of water (1:1) in both cases, indicating that the water induces carbocation chemistry. The proportion of saturated hydrocarbons increased with time at the expense of unsaturated hydrocarbons, suggesting alkylation and/or hydrogenation reactions. Among the higher molecular weight hydrocarbons (C14-C34), there was a strong predominance (55-60%) of $\text{C}_{21}\text{H}_{44}$, the direct decarboxylation product of behenic acid.

Johns¹¹ studied kinetically the decarboxylation of behenic acid using a series of clays under anhydrous conditions. Arrhenius plots of the data show large decreases in activation energy (from 58.4 to 24.7 kcal/mol) for decarboxylation in the clay-catalyzed reactions compared to the reaction without clay catalysis. The effects of these catalysts were shown dramatically, by calculating the time required for 90% decarboxylation at 60 °C, which ranged from 2.9×10^{50} years for the thermal conversion to only 0.03 year (11 days) when nontronite, an iron-containing clay, was present. Johns points out that the catalytic activity measured in these laboratory studies surpasses that of the natural shale kerogen systems, a finding partially explained by the sharp decrease in clay acidity with increasing water content.

Frenkel and Heller-Kalai¹² demonstrated that the main reaction of the low molecular weight terpene, limonene (VII), in the presence of montmorillonites, is conversion to the aromatic hydrocarbon *p*-cymene (VIII) and to *p*-menthane (IX) and *p*-menthene (X), demonstrating that kerogens could be converted by surface-active materials in sediments to low molecular weight aromatic compounds of the type found in petroleum. A subsequent study by Goldstein¹³ showed that geraniol (VI), a biologically synthesized unsaturated alcohol, undergoes stepwise catalytic conversion in the presence of water, clays, and other sediments at <100 °C initially to form polymeric materials. These polymeric materials were converted into the more thermodynamically stable phenyl, naphthyl, and higher condensed aromatic products. This model system study nicely demonstrates that clay, limestone, and other sediments catalyze a wide variety of reactions in closed, water-containing systems of varying pH (3.9-9.7).

In addition, several other studies have considered the reaction of resource materials (kerogens) in hot water as an alternative to anhydrous pyrolysis at higher temperature. Simulation of petroleum formation required hydrous conditions because water is ubiquitous in sediments. Winters et al.¹⁴ demonstrated that the characteristic low olefin (high saturates) content of natural petroleum oils could be produced by hydrous pyrolysis of Woodford (Devonian), Phosphoria (Permian), and Kimmeridge (Jurassic) source rock shales at 330 °C. Thus, hydrous pyrolysis in a closed system appeared to be a more realistic reaction system than anhydrous pyrolysis in an open system which, by contrast, generates large amounts of olefins. This work is complemented by that of Tannenbaum and Kaplan¹⁵ who carried out a comparative study in which low molecular weight hydrocarbons were generated from Green River oil shale kerogen by both hydrous and anhydrous pyrolysis. At 300 °C, production of initial C2-C6 olefins was comparable in both systems, but under aqueous conditions, their concentrations then started to decrease with time (also observed by Jurg and Eisma¹⁰). This high reactivity of the olefins may explain why olefins were not previously observed under hydrous conditions.

The hydrous pyrolysis¹⁶ of a benzene-methanol extracted Messel shale at 330 °C for 3 days in the presence of D_2O gave saturated hydrocarbon products multiply (1-14) substituted by deuterium. Heating the saturated hydrocarbon docosane ($\text{C}_{22}\text{H}_{46}$) with a sample of solvent-extracted shale in an excess of D_2O showed only minor deuteration of the re-isolated docosane (80%). This result suggested that simple hydrogen exchange on saturated molecules can be ruled out as a major pathway. However, under similar conditions in the aqueous system, the olefin 1-octadecene was completely reduced to octadecane (60%) with simultaneous significant deuterium incorporation. Hoering applied similar treatment to a kerogen- 2-ethylheptadecanoic

acid mixture and found that the acid decarboxylated to 2-methylheptadecane in 10% yield, while facile deuterium exchange took place at hydrogen atoms adjacent to (α -to) oxygenated functional groups. In other studies, Hoering and Abelson¹⁷ showed that deuterated hydrocarbons are generated from kerogen heated in D₂O at 100 °C and then dried and pyrolyzed in an inert atmosphere. They proposed that olefins, or olefin intermediates generated during pyrolysis, exchanged with the D₂O. Alexander et al.¹⁸ found considerable exchange of isotopic hydrogen between naphthalenes and the acidic clay surfaces, at 23 °C, or in aqueous slurries at 70 °C.

Eglinton et al.¹⁹ carried out the hydrous pyrolysis of a Kimmeridge kerogen (Type II) at 280 or 330 °C for 72 h in the presence of clay or carbonate minerals. They found that more organic-soluble pyrolyzate was formed when calcium carbonate was the inorganic phase, which suggests significant base catalyzed cleavage of cross-links.

Graff and Brandes²⁰ found that a steam pretreatment of an Illinois bituminous coal (Type III kerogen) between 320 and 360 °C dramatically improved the yield of liquids upon subsequent conversion or solvent extraction. The steam-modified coal contains twice the hydroxyl groups of the raw coal. This leads to the conclusion that steam reacts with the ether linkages in coal, forming hydroxyl groups, and thereby substantially reducing an important covalent cross-link in the coal structure.²⁰ These conclusions are consistent with model compound studies on ether reactivity in hot water.^{1,20,21}

Aqueous Cleavage/Hydrolysis Reactions

1. Neutral Reactions

Rapid and clean ring cleavage of the cyclic aromatic ether 2,5-dimethylfuran in pure deuterium oxide at 250 °C yielded 2,5-hexanedione quantitatively and irreversibly within 30 min.²² the 2,5-hexanedione product undergoes no ring closure at this temperature in 1 h. These reaction conditions are in contrast to those reported in a mechanistic study of this reaction, in which a 0.1M DCl solution at 70 °C was required to cleave the ring.²³ Dibenzofuran¹ and 2-hydroxydibenzofuran²⁴ proved to be stable to aquathermolysis even at 460 °C.

Acetals and ketals are highly reactive to neutral aquathermolysis, undergoing in nearly all cases 100% hydrolysis within 30 min at 205-250 °C without side or secondary reactions.²² Greater than 90% deprotection of cyclopentanone ethylene ketal and 1,4-cyclohexanedione bis-(ethylene ketal) was achieved at 250 °C. Equal reactivities to pure water were determined for benzaldehyde and tolualdehyde diethyl acetals at 186 and 250 °C resulting, during 30 min reaction, in 91-94% and 100% conversion, respectively. Hydrolysis of benzaldehyde diethyl acetal went to completion overnight at room temperature but decreased to 33% in the presence of basic barium oxide at 80 °C over 45 min. At 254 °C, quantitative hydrolysis of this acetal in aqueous KOH at acetal:base molar ratios as low as 1:0.25 (72.5 mM in KOH) was followed by a Cannizzaro disproportionation, as indicated by the formation of benzyl alcohol, benzoic acid, and, via subsequent decarboxylation of the acid, small amounts of benzene. Formation of Cannizzaro products of benzaldehyde in the presence of a much weaker base, pyridine, was reported previously.²⁵ Tsao and Houser suggested the possibility of a Cannizzaro reaction of this aldehyde catalyzed by ammonia in supercritical water, but, product distributions indicate the involvement of radical pathways.²⁶

Diacetone-D-glucose (0.31 M) and 1,6-anhydro- β -D-glucose (0.30M) were converted quantitatively at 205 °C to predominantly D-glucose and traces of another glucose isomer.¹⁶ Under the same conditions in the presence of 1 equivalent of KOH (0.29 M), 1,6-anhydro- β -D-glucose was unreactive and only the exocyclic, 5,6-acetone moiety of diacetone-D-glucose was cleaved. Cellulose is rapidly converted to soluble species with relatively high glucose yield in pure water near its critical temperature.²⁷ In a semi-batch or flow reactor, 100% conversion of cellulose was achieved in 1 h or less (15 sec at 400 °C). Parallel thermal transformations of the glucose product take place to form fructose, 1,6-anhydro D-glucose, erythrose, glycolaldehyde, glyceraldehyde, dehydroxyacetone, pyruvaldehyde, and acids.

2. Other Cleavage Reactions

The thermally stable ester, methyl 1-naphthoate is quantitatively hydrolyzed after 2 h and 5.5 day treatments at 343 and 250 °C, respectively.¹ Naphthoic acid is the major product at 250 °C, but its decarboxylation led predominantly to the formation of naphthalene during a 2 h conversion at 343°C; a reaction catalyzed by the generated carbonic acid. Examinations of methyl benzoate and its 4-chloro, 4-methyl, and 4-methoxy derivatives revealed up to 50% hydrolysis within 30 min at 250°C,²² but no evidence of decarboxylation. Partial cleavage of the *p*-methoxy group is assumed to be caused by the increased acidity of the medium resulting from carboxylic acid formation, since no ether cleavage was observed for α -ethyl-4-methoxybenzyl alcohol, in neutral water under otherwise more extreme conditions (277 °C, 75 min). Aliphatic 1,1-dicarboxylic acids are more reactive and Brill followed the decarboxylation of 1.07 M malonic acid to CO₂ and H₂O and the slower decarboxylation of monosodium malonate to CO₂ and acetate ion at 120-230 °C and 275 bar.²⁸ In a reaction typical of β -keto esters, ethyl

acetoacetate underwent complete conversion to acetone, ethanol, and CO_2 (not analyzed) in 30 min at 250°C .²² Under similar conditions, *tert*-butyl acetate decomposed to a bright red, highly insoluble mixture of unidentified products resulting from polymerization of isobutylene;¹³ but methyl trimethylacetate was unreactive.

Cyclohexyl-*x*-phenyl compounds, characteristic of structures found in Type II Kimmeridge shales, with oxygen, sulfur, and nitrogen links were shown to be relatively unreactive thermally but readily cleaved in water at 250°C to form methylcyclopentene together with phenol, thiophenol, or aniline, respectively (Eq 5).²¹

Ionic reactions of these types are enhanced in 10% NaCl (acting as a weak acid) and in the presence of an acidic clay, but are depressed by basic calcium carbonate. This evidence supports an acid-catalyzed carbocation mechanism for this system in water at high temperature. Although an acyclic diaryl ether (diphenyl ether) and a cyclic diaryl ether (dibenzofuran) were unreactive under both aqueous and thermal conditions, an activated diaryl ether (4-phenoxyphenol) was cleaved in water to form phenol (Eq 6).¹ Penninger and Kolmschate treated 2-methoxynaphthalene with supercritical water at 390°C for 1.5 h to give 2-naphthol and methanol as main reaction products.²⁹ Benzyl aryl ethers were also much more susceptible to cleavage under aqueous than thermal conditions at 250°C . Klein reported that phenethyl phenyl ether formed phenol and styrene as the primary products after 1 h at 400°C and dibenzyl ether yielded benzyl alcohol, toluene, and benzaldehyde after treatment in water at 374°C for 1 h.³⁰

The thermally stable diaryl ether 1-phenoxy-naphthalene is cleaved in water at 315°C after three days to phenol and 1-naphthol (95% conversion) and is thus significantly more reactive than diphenyl ether.³¹ In aqueous sodium formate reduction of the 1-naphthol to naphthalene and dihydronaphthalenes occurs. 9-Phenoxyphenanthrene similarly yields phenol and 9-hydroxyphenanthrene (Eq 8) and is more reactive than its 1-phenoxy isomer.³² Interestingly, the rate of hydrolysis of such diaryl ethers is affected dramatically by additives such as NaCl, LiCl, KBr, and Na_2SO_4 .³³ The conversion of 1-phenoxy-naphthalene in water alone at 315°C after 72 hours was 94.6%; on reaction of this substrate with a 1% aqueous solution of each of the above salts, the conversion was reduced to 7.4%, 4.8%, 3.8%, and 0%, respectively. These results strongly suggest that at high temperatures, alkali metal halides and sodium sulfate behave as salts of strong bases and weak acids and reduce the hydrogen ion activity of the solutions, in agreement with previous indications.³³

Hydrogen Exchange Reactions

When the ring cleavage reaction of 2,5-dimethylfuran was conducted in deuterium oxide,³⁴ extensive deuteration of the methyl and methylene groups in the product, 2,5-hexanedione, was observed; the same result was detected by ^1H and ^{13}C NMR when this dione was the initial reagent. Thus, it became evident that this medium was suitable for $^1\text{H}/^2\text{H}$ exchange.²² These exchange reactions afforded an additional means to study organic transformations in a reaction environment undergoing minimal changes; for example, no products are formed that have significantly different properties or reactivities from those of the initial reagents. Also, no changes occur in reaction mechanisms, volume, vapor pressure, or the dielectric or dissociation constants of deuterium oxide because of the formation of ionic products and potential catalysts or co-solvents.

Deuterium oxide treatment of methyl (300°C , 93 h), isopropyl, and neopentyl alcohol (200°C , 30 min and 300°C , 60 min, respectively) did not induce any exchange of C-H hydrogens; the same negative results were obtained in experiments with ethylene glycol (300°C , 60 min) and pentaerythritol (250°C , 60 min).²² Hydrogen exchange was achieved rapidly and nearly quantitatively in the α and α' (where applicable) positions of ketone carbonyl groups. Table 2 lists the extents and sites of deuteration observed in selected ketones. In all cases, the operating enol-keto tautomerism led exclusively to hydrogen exchange; no aldol products were observed.

Table 2. Hydrogen/Deuterium Exchange in Ketones

Compound	% D (position)	Reaction Conditions	
		°C	Min
Pinacolone ^a	100 (α CH ₃)	277	60
Acetone	97 (α , α' CH ₃)	200	60
Cyclopentanone ^b	100 (α , α' CH ₂)	225	30
1,4-cyclohexanedione	100 (α , α' CH ₂)	225	30
Acetophenone	>88 (α CH ₃)	250	60
Deoxybenzoin ^c	99 (α CH ₂)	250	30

a Exchange observed in the rearrangement product of pinacol.

b Exchange observed in the hydrolysis product of the corresponding ethylene ketal.

c PhCH₂COPh.

Nearly quantitative exchange by reaction with only 0.016M sodium deuteroxide solution for 10 min at 400 °C and ~300 bar pressure occurred for molecules having pK_a's up to approximately 43, while longer heating time and more concentrated base solutions allow deuteration of still more weakly acid compounds having pK_a's up to 50.³⁵

Technological Applications

Chemical reactions carried out in hot water have the potential to provide a cleaner, safer environment than reactions in hydrocarbon solvent media. In addition, water acting as a catalyst or reagent could minimize, or possibly eliminate, the need for catalyst synthesis, recycle, regeneration, and disposal. Such application to the recycle of condensation polymers including plastics, synthetic fibers, and polycarbonates is attractive.^{2,36} Another potential application is the use of hot water treatment to upgrade low-value by-products. A demonstrated example occurs in the hydration of propylene with sulfuric acid to form isopropyl alcohol with thermally stable diisopropyl ether as a by-product. Hydrous cleavage of this by-product ether at 315 °C for 30 min readily forms essentially equimolar amounts of the desired product (isopropyl alcohol) and recyclable propylene.³⁷ Di-*sec*-butyl ether, a by-product in the hydration of butylene to *sec*-butyl alcohol in the methyl ethyl ketone (MEK) process, can similarly be converted to the alcohol in hot water³⁷ (Eqs 9 and 10). The aldol condensation by-product of MEK production, a C₈-unsaturated ketone, is quantitatively reversed to MEK by hydration followed by retro-aldol cleavage.³⁸

CONCLUSIONS

This article describes the reactivity of organic molecules in superheated water. Emphasis was placed on the geochemical perspective because, outside of biological processes, where aqueous chemistry predominates and is catalyzed by enzymes, kerogen formation and its subsequent depolymerization into petroleum is the major arena in nature where aqueous chemistry is observed. In this chemistry, water participates as catalyst, reactant, and solvent. While the geochemical aspects serve as a foundation for understanding the aqueous chemistry, the implications for a wide variety of other organic chemical transformations and technological applications are potentially large and just beginning to emerge. The unique ability of water to carry out condensation, cleavage, and hydrolysis reactions and provide an opportunity (not accessible thermally) to effect selective ionic chemistry, is largely due to changes in the chemical and physical properties of water, which become more compatible with the reactions of organics as the temperature is increased. Therefore, its solvent properties at 250-350 °C approach that of polar organic solvents at room temperature. It can act as an acidic or basic catalyst and its reactivity can often be reinforced by autocatalysis from water soluble reaction products generated. Additional positive aspects of the use of aqueous chemistry are its simplicity, low cost, and favorable environmental impact.

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Figure 1

**EXAMPLE OF KEY CLEAVABLE LINKAGES IN RESOURCES ...
... RUNDLE RAMSAY CROSSING OIL SHALE KERGEN**

